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27 June 2001

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Ghanshyam L. Vaghjiani, "Investigations of Chemiluminescence in the CH<sub>2</sub> + O Gas Phase Reaction"

**37<sup>th</sup> AIAA/ASME/SAE/ASEE JPC & E** (Statement A)  
(Salt Lake City, UT, 08-11 Jul 2001) (Deadline: 30 June 2001)

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Space and Missile Propulsion Division

Date



**AIAA-2001-3710**

## **Investigations of Chemiluminescence in the CH<sub>2</sub> + O Gas Phase Reaction**

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INVESTIGATIONS OF CHEMILUMINESCENCE IN THE  $\text{CH}_2 + \text{O}$  GAS PHASE REACTION

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## ABSTRACT

The reaction of ketene ( $\text{C}_2\text{H}_2\text{O}$ ) in a known excess of O-atoms was studied in a discharge flow-tube apparatus. Characteristic CO-chemiluminescence was observed in the range 130-900 nm. The rate coefficient for this reaction was determined to be  $(6.82 \pm 1.02) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  at 295 K by recording the relative strength of the steady-state 216-nm Cameron emission as a function of the reaction length in the flow-tube. The band structure of the emission spectrum recorded suggests that the subsequent very rapid reaction of O-atoms with the product,  $\text{C}_2\text{O}$  and possibly with  $\text{CH}_2$ , that are formed in the initial  $\text{C}_2\text{H}_2\text{O} + \text{O}$  oxidation lead to the observed radiation. 351-nm pulsed laser photolysis of the unreacted ketene in the detection volume of the apparatus resulted in transient enhancements of the CO-chemiluminescence. The time behavior of these emissions and their dependence on the laser fluence employed was consistent with the photolytic production of  $\text{CH}_2$  and also  $\text{C}_2\text{O}$ , respectively, due to 1-photon and 2-photon absorption of the 351-nm laser radiation by the ketene. Strong  $\text{OH}(\text{A})$  emission was also seen in these experiments when excess  $\text{O}_2$  was present. The reaction of  $\text{CH}$  with  $\text{O}_2$  is responsible for this emission. The principal source for  $\text{CH}$  in our system is thought to be the  $\text{CH}_2 + \text{O}$  reaction.

INTRODUCTION

The interactions of carbonaceous combustion species in rocket plumes with the atmosphere are thought to play an important role in the production of ultraviolet, visible, and infrared radiation signatures at high altitudes. A detailed understanding of the pertinent chemical reactions that produce the electronically excited species, and of the competing quenching reactions that remove the internal energy in radiation-less processes is needed to accurately calculate short wavelength plume spectral signatures and absolute radiances and their temporal/spatial evolution in the high atmosphere. To facilitate these efforts, we are currently carrying out laboratory investigations to elucidate the reaction mechanisms in the oxidation of  $\text{CH}$ ,  $\text{CH}_2$ ,  $\text{C}_2\text{H}$ , and  $\text{C}_2\text{O}$  with O-atoms and  $\text{O}_2$ . Sufficient exothermicity in  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{C}_2\text{H}$  reactions (except  $\text{C}_2\text{H} + \text{O}$ ) is available to produce CO in one or more of the triplet states (a, a', and d).

Even more reaction enthalpy is available in  $\text{C}_2\text{O}$  reaction(s) to produce higher excited states of CO (e, A, I, and D). Other excited species such as  $\text{CH}(\text{A}^2\Delta)$  in  $\text{C}_2\text{H} + \text{O}$  (or +  $\text{O}_2$ ), and  $\text{OH}(\text{A}^2\Sigma^+)$  in  $\text{CH} + \text{O}_2$  reactions are also possible. uv-CO-chemiluminescence has previously been identified in the  $\text{C}_2\text{H} + \text{O}_2$  reaction,<sup>1</sup> and both uv- and vuv-CO-chemiluminescence in the  $\text{C}_2\text{O} + \text{O}$  reaction.<sup>2-7</sup> However, only limited information is available on the product branching ratios of the excited CO states responsible for the emission.<sup>7</sup> Estimates of the branching ratio of  $\text{CH}(\text{A}^2\Delta)$  formation in the reactions of  $\text{C}_2\text{H}$  with O and  $\text{O}_2$  can be found in the literature.<sup>8-10</sup> To our knowledge, triplet CO formation in  $\text{CH}$  and  $\text{CH}_2$  reactions has not yet been positively identified. Fast discharge-flow tube and pulsed-laser photolysis methods have been employed in this work to study the reaction kinetics and chemiluminescence in these and  $\text{C}_2\text{O}$  reactions.

## EXPERIMENTAL TECHNIQUE

The discharge flow-tube apparatus employed in this work has previously been described in detail elsewhere.<sup>11</sup> A schematic of the apparatus is shown in Figure 1. Here, we only provide details of the experimental procedures employed to record the chemiluminescence data. A small flow of  $C_2H_2O$  in helium was carried into an absorption cell for 213.9-nm photometric determination of its gas phase concentration before sending it for further dilution via a sliding injector into the main reaction section of a flow-tube that carried a known excess flow of He. A value of  $\sigma_{213.9\text{ nm}} = 889.2 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$  was used for the  $C_2H_2O$  uv-absorption cross-section.<sup>12</sup> A fixed side-arm microwave discharge port was used to introduce an excess of  $O(^3P)$  into the flow-tube.  $O(^3P)$  was made from the discharge of a 1% mixture of either  $O_2$  or  $N_2O$  in He. The  $[O(^3P)]$  in the flow-tube was determined by  $NO_2$  titration;  $O + NO_2 \rightarrow NO + O_2$ . The end-point of this reaction was followed either by monitoring the yellowish-green emission in the accompanying,  $O + NO \rightarrow NO_2 + h\nu$  reaction, or by direct vuv cw-resonance fluorescence detection of the  $O(^3P)$ . The electronic mass flow meters, capacitance manometers and the chromel-alumel thermocouples used to flow the gases, and measure the flow-tube system's pressure and temperature had previously been calibrated. A typical linear velocity,  $v = 800 \text{ cm s}^{-1}$  for the bulk flow rate of the He gas was maintained through the 1-inch-diameter flow-tube at a nominal pressure of 2.0 Torr to ensure that the flow-tube was being operated under plug-flow conditions at the ambient temperature of 295 K.<sup>13</sup> For the data reported here, the  $[O(^3P)]/[C_2H_2O]$  ratio ranged from 20 to 200, where the  $[O(^3P)]$  was between  $(3.5-23.5) \times 10^{13} \text{ molec cm}^{-3}$ .

The steady-state chemiluminescence produced when  $C_2H_2O$  interacted with the O-atoms at a fixed reaction length,  $z$ , in the flow-tube was observed downstream at the detection zone using 2 suitable scanning monochromator/PMT detector assemblies that covered the entire 130-900 nm range of interest. Signals from the PMTs were analyzed using photon-counting/multi-channel averaging techniques.<sup>14</sup> The instrument resolutions were  $\sim 1.9$  and  $\sim 1.1 \text{ nm, FWHM}$ , respectively, in the uv and the visible portions of the spectrum. Suitable cutoff filters were placed at the entrance slit of the monochromator to avoid detection of the uv radiation through second order transmission when recording in

the visible region. Figures 2, 3, 4, and 5 show the typical emissions observed. The kinetics of this reaction was followed by recording the relative strength of the 216-nm emission as a function of the reaction length in the flow-tube for a series of chosen O-atom concentrations. Figure 6 shows the exponential dependence of the emission intensity with the reaction time,  $t = z/v$ .

A 351-nm pulsed laser beam (20-50 mJ/pulse and operating at 10 Hz) was focused at the detection zone to photolyze any unreacted ketene to look for transient enhancements in the CO-chemiluminescence at a selected few emission band centers. A 10- $\mu$ sec dwell-time was employed in the multi-channel averager to properly resolve the time profile of the transient emissions. The time behavior of the transient signal was recorded by co-adding typically 50000 pulses to improve the signal-to-noise ratio of the data. Figures 10, 11, and 12 show the transients recorded at 788, 216, and 165 nm.

## Materials

He (>99.9997%) carrier gas from U. S. Bureau of Mines was used as received.  $NO_2$  (99.9%) from M. G. Scientific Gas was mixed with excess  $O_2$  to react away any NO present and the mixture collected in a trap over silica gel at 213 K. The excess  $O_2$  and any other volatiles were pumped off and the condensate subjected to several freeze-thaw purification cycles at a greaseless vacuum line. A standard 10%  $NO_2$  in He titration mixture was prepared.  $O_2$  (99.991%) from Big Three Industries and  $N_2O$  (99.99%) from Matheson Gas Products were used as supplied to make up 1% in He discharge mixtures. Ketene was prepared by pyrolytic decomposition of acetone (HPLC grade) over a heated (970-1020 K) Chromel-A wire in a reflux apparatus. The effluents from the apparatus were first passed through a trap maintained at 270 K to remove most of the unreacted acetone, and then through another trap maintained at 173 K to collect the ketene. The condensate was subjected to several freeze-thaw purification cycles to remove the remaining acetone and any  $CO_2$  collected during the synthesis. The uv spectrum of the purified sample was measured in the range 140-400 nm.<sup>12</sup> No characteristic acetone absorption features were seen. The sample purity of the ketene was estimated to be  $\sim 99\%$  from the calculated absorption cross-sections. A 10% ketene in He reaction mixture was prepared.

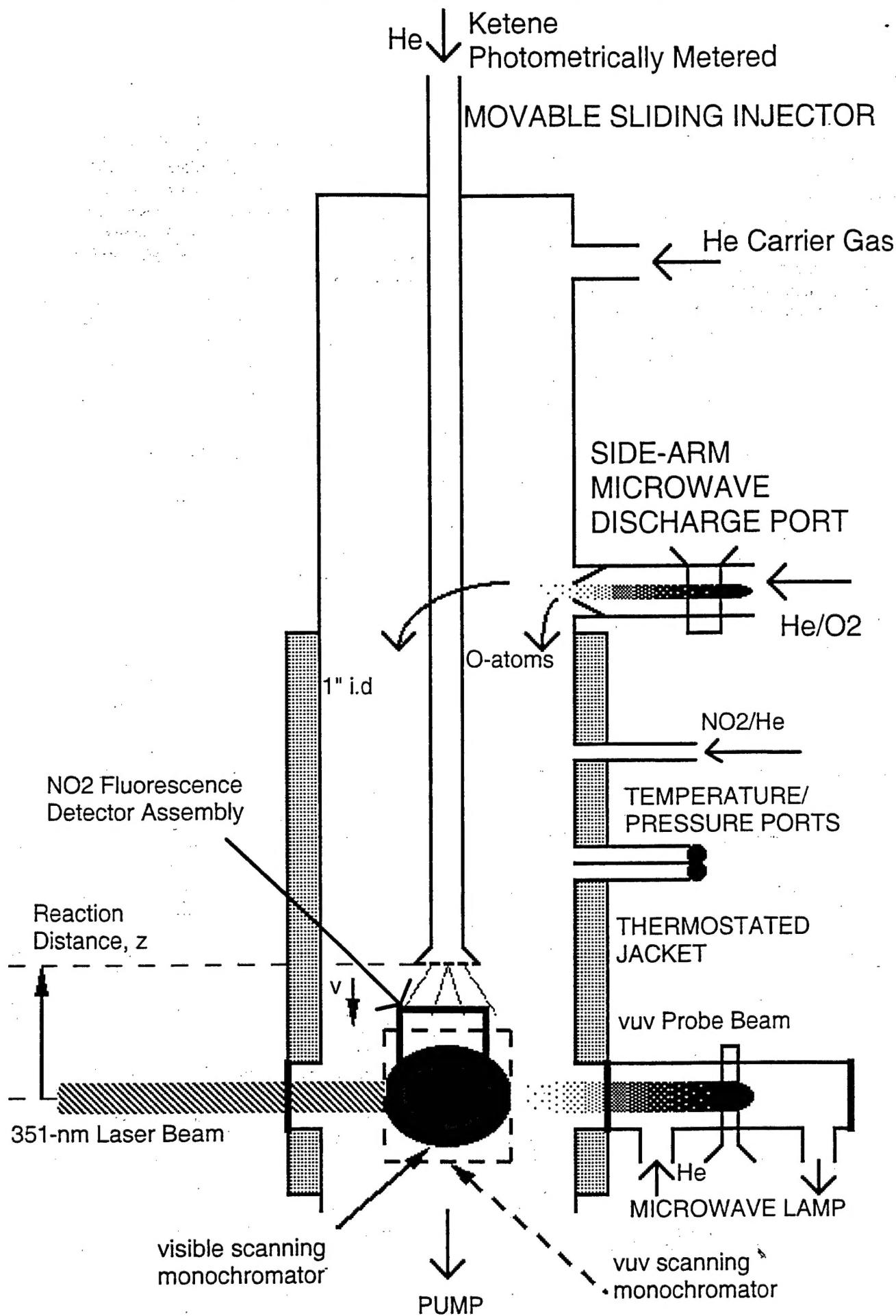


FIG. 1. Discharge flow-tube/pulsed photolysis apparatus.

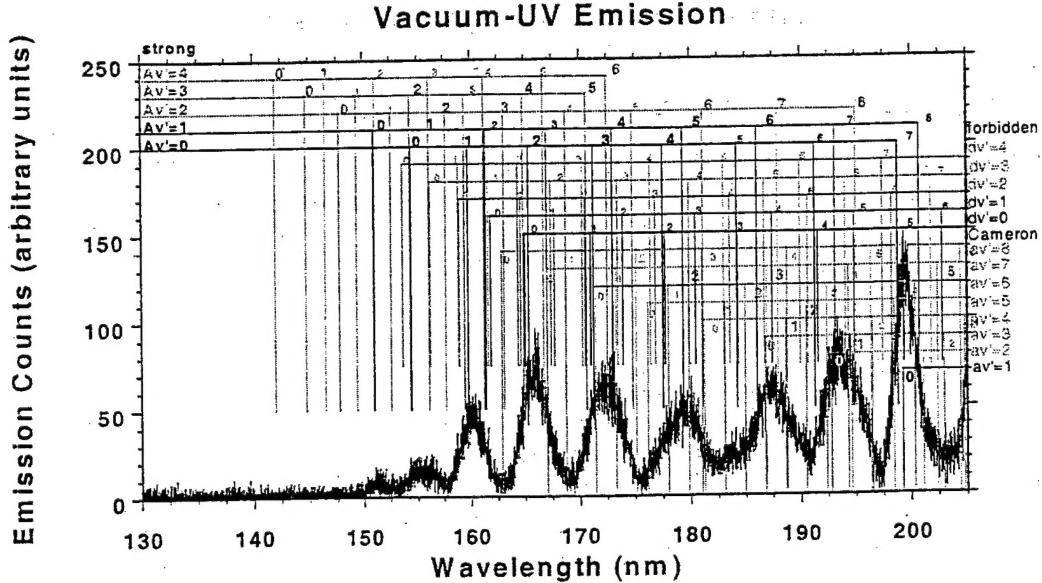


FIG. 2. vuv-CO-chemiluminescence observed during  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  reaction.

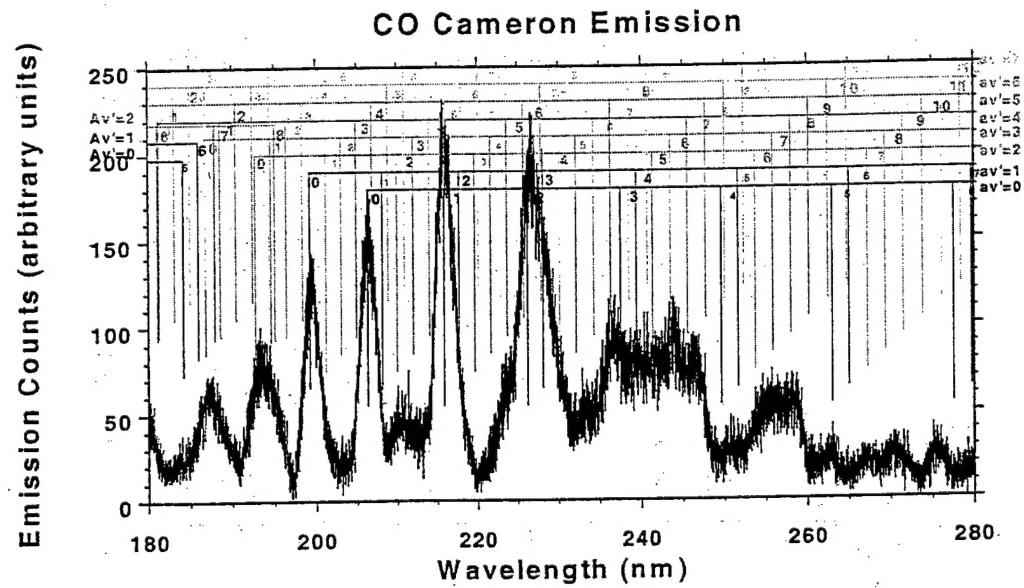


FIG. 3. uv-CO-chemiluminescence observed during  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  reaction.

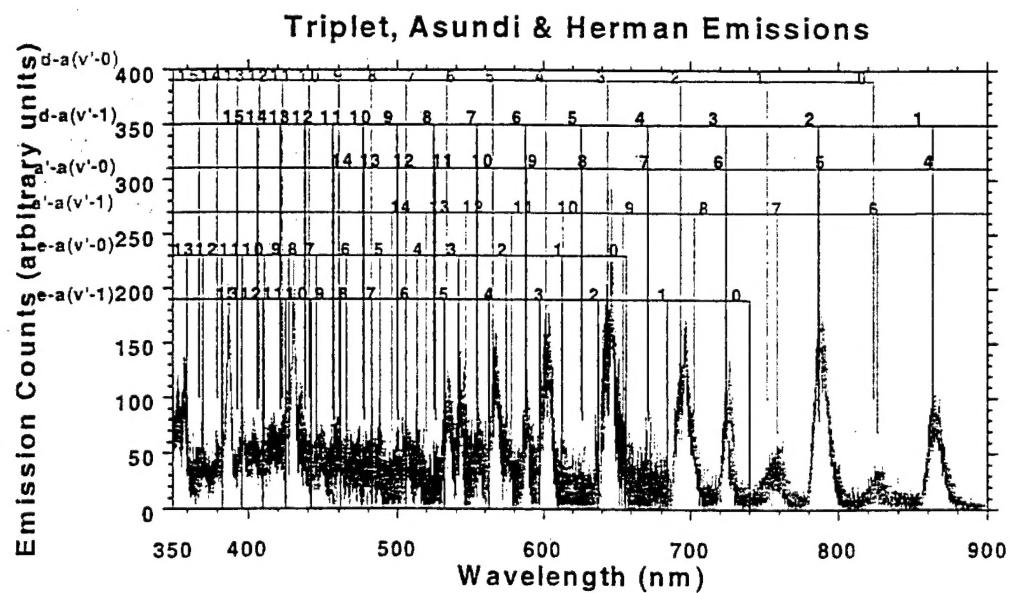


FIG. 4. Visible-CO-chemiluminescence observed during  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  reaction.

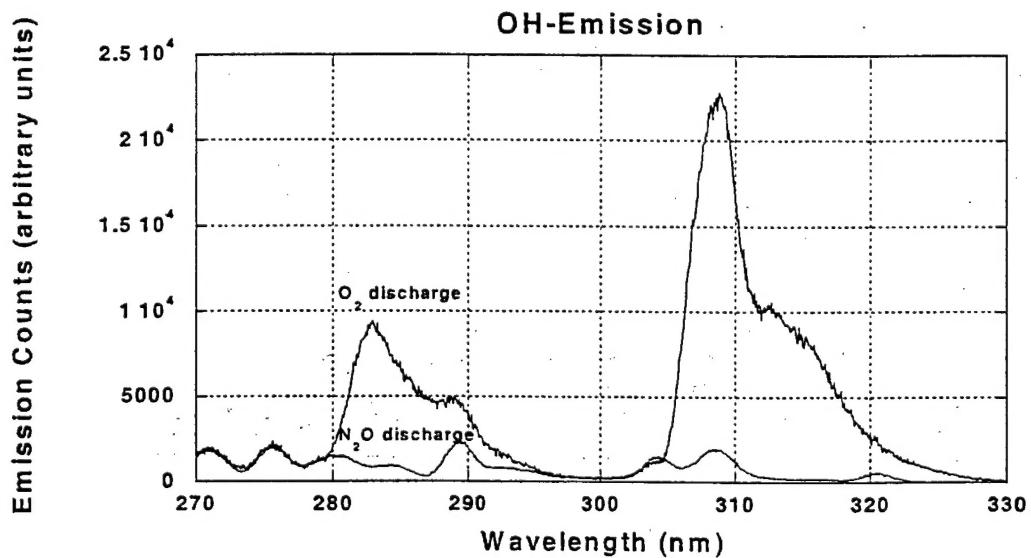


FIG. 5. uv-OH-chemiluminescence observed during  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  reaction.

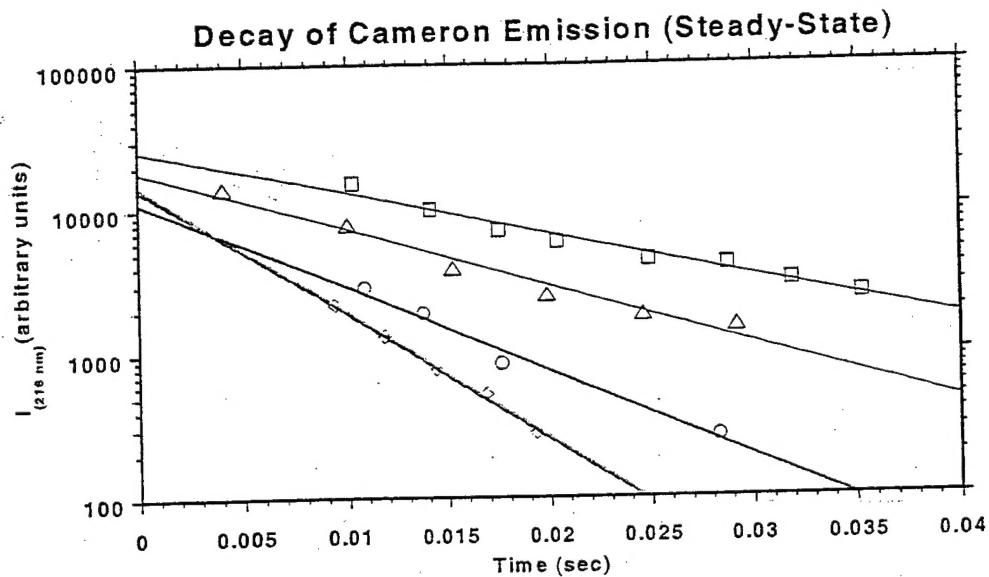


Fig. 6. Decay of 216-nm-CO-emission as a function of flow-tube reaction time for four different O-atom concentrations.

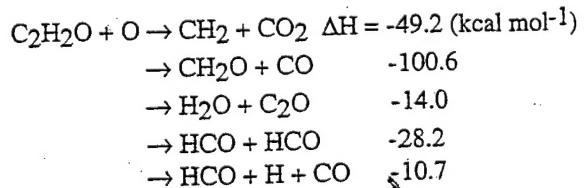
## RESULTS AND DISCUSSION

### Flow-tube work

Even though CO may form directly in the  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  interaction, the reaction exothermicity is insufficient to produce the electronically excited product. Thus, the source of emission in Figures 2, 3, and 4 must be from the subsequent reaction of excess O-atoms with the product(s) in this reaction. If the oxidation rate of ketene by O-atoms is much slower (and therefore rate limiting) compared to that of the product(s), it can be shown that the steady-state emission strength in the flow-tube for long reaction times will follow an exponential relationship with a decay coefficient given by  $k' = k + k_1[\text{O-atom}]$ .  $k'$  is the pseudo-first-order loss rate term for  $\text{C}_2\text{H}_2\text{O}$  in the flow-tube, where  $k$  is the loss rate term in the absence of O-atoms, and  $k_1$  the absolute second-order rate coefficient for  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  reaction. Figure 6 shows how the 216-nm emission, due to the  $\text{CO}(a, v' = 0 \rightarrow X, v'' = 1)$  transition, varied as a function of the reaction time in the flow-tube for different O-atom concentration conditions. The straight lines are

exponential fits to the data points where the slopes yield values for the first-order loss rate terms for  $\text{C}_2\text{H}_2\text{O}$ . In Figure 7 these values are plotted as a function of the [O-atom] employed to extract the second-order rate coefficient from the fit of the data points to a straight line. A value of  $k_1$  equal to  $(6.82 \pm 1.02) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  at 295 K was determined. This value is in excellent agreement with previous determinations by Carr and co-workers ( $8.8 \times 10^{-13}$ ),<sup>15</sup> Mack and Thrush ( $5.7 \times 10^{-13}$ ),<sup>16</sup> and Washida and co-workers ( $4.3 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ).<sup>17</sup>

The possible products in the ketene plus O-atom reaction are shown below:



Mack and Thrush<sup>16</sup> did not observe any significant amount of water formation in their work.

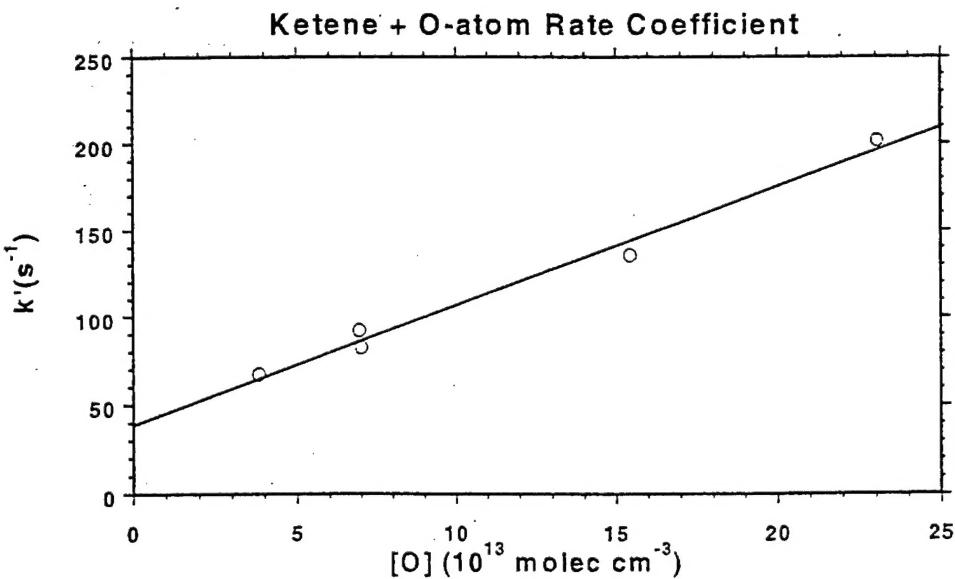
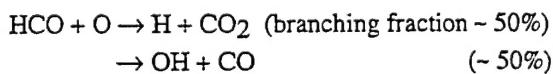
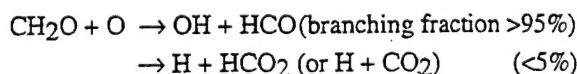


FIG. 7. A plot of  $k'$  versus  $[O]$  employed in Figure 6.

Therefore the formation of  $C_2O$  (the co-product in the third channel) is expected to be negligible in this reaction. Carr and co-workers<sup>15</sup> and Washida and co-workers<sup>17</sup> have directly determined the formaldehyde yield to be ~ 20% and ~ 15%, respectively. The latter group also directly determined the total  $HCO$  yield to be ~ 10%. Thus the second, fourth, and fifth channels are also minor processes in ketene oxidation by O-atoms. Furthermore, the product studies of Mack and Thrush also showed a high yield for  $CO_2$ .<sup>16</sup> However, they rationalized this to be due to the subsequent oxidation of the formyl radical, which they assumed to be the dominant initial product in their experiments:



The  $HCO$  can also arise from subsequent formaldehyde oxidation:



One can reconcile the differences of these two studies by proposing the first channel to be the dominant source of  $CO_2$ . This would imply that  $CH_2$  is a major product in the ketene + O-atom reaction. The reaction of  $CH_2 + O$  is known to be very fast<sup>18</sup> and exothermic enough (by ~ 179.3 kcal mol<sup>-1</sup>) to possibly excite the known  $CO$  product into its triplet states. We should then expect to see Cameron emissions from  $CO(a, v' \leq 8)$ , Asundi emissions from  $CO(a', v' \leq 6)$ , and Triplet emissions from  $CO(d, v' \leq 1)$  in the room temperature ketene plus O-atom reaction. The data of Figures 4 and 2, however, show emissions arising from even higher levels. There are two possibilities for this in our apparatus. One is that the  $C_2H_2O + O$  reaction produces internally excited  $CH_2$ . The 49.2 kcal mol<sup>-1</sup> of energy available could allow vibrationally excited  $CH_2(^3B)^{\pm}$  to be formed with up to ~ 9.0 kcal mol<sup>-1</sup> of internal energy. Excitation in excess of this would promote the methylene (directly or in energy transfer collisions) into the first excited singlet ( $^1A$ )-state, which would rapidly quench back to the ( $^3B$ )-state under our flow-tube conditions.

If excited  $CH_2(^3B)^{\pm}$  reacts with the O-atoms,  $CO(A, v' = 0)$  formation would be possible.

This would predict the shortest, 4<sup>th</sup>-Positive, CO-emission wavelength of  $\sim 151.8$  nm in the vacuum-uv. Of course, correspondingly higher  $v'$  excitations in (a), (a') and (d) triplet states would also occur compared to that in the ground-state reaction of  $\text{CH}_2(^3\text{B})$ . However in Figure 2, we still see emission to the blue of this threshold, which implies that yet another species' reaction with O-atoms is important in our system. The most likely candidate for this is the  $\text{C}_2\text{O} + \text{O-atom} \rightarrow \text{CO} + \text{CO}^*$  reaction, which would have an emission threshold at  $\sim 139.7$  nm. In Figure 8 the data of Figure 2 is re-plotted on a logarithmic scale in the region 130-165 nm. The non-zero signal for wavelengths shorter than 139.7 nm possibly indicates the involvement of internally excited  $\text{C}_2\text{O}$ . The data below  $\sim 146$  nm is unresolvable with the present spectrometer resolution

which was chosen so as to have sufficient throughput for enough detection sensitivity (i.e.,  $\text{S/N} = 1$ , for 1-second integration) and at the same time be able to resolve the broader and stronger bands in the long wavelength region.

We are currently investigating<sup>19</sup> the direct LIF-detection of  $\text{C}_2\text{O}$  formation in our  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  flow-tube setup to confirm the above explanation for the source of high-energy vuv-emissions we have observed. In the next section we describe the results of a pulsed photolysis approach we have used to form transient amounts of  $\text{CH}_2$  from ketene photodissociation at 351 nm<sup>20</sup> to see if CO-chemiluminescence can be uniquely assigned to the  $\text{CH}_2 + \text{O-atom}$  reaction.

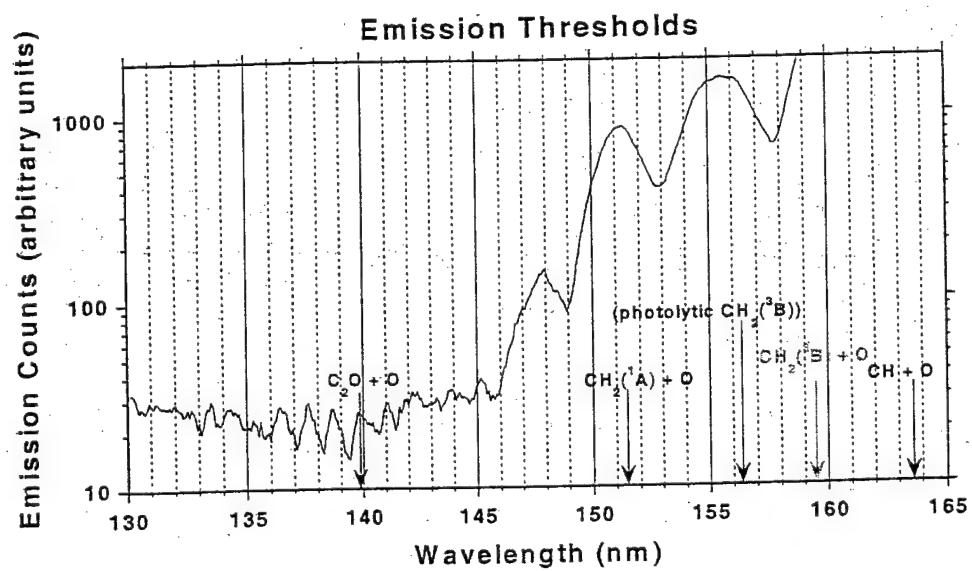


FIG. 8. Comparison of the vuv-emission spectrum obtained in this work to expected emission thresholds for various possible reactions of carbonaceous species with O-atoms in our flow-tube.

In addition to the CO-chemiluminescence, characteristic OH(A) emissions in the (1 $\rightarrow$ 0), (0 $\rightarrow$ 0), and (1 $\rightarrow$ 1) bands were also seen when  $\text{O}_2$  was present, i.e., when an  $\text{O}_2$ -discharge source was used

to produce the O-atoms. It is known that in this source, typically 80-90% of the  $\text{O}_2$  remains undisassociated. When a  $\text{N}_2\text{O}$ -discharge source was used to produce the O-atoms no OH emission was

seen (see lower trace in Figure 5, which shows only the underlying CO-emissions in this region). However, in this case, when a small amount of O<sub>2</sub> was deliberately added to the flow-tube via a side-inlet, strong OH(A) emissions ensued. The following mechanism is proposed for the observed emission. The CH<sub>2</sub> produced in the C<sub>2</sub>H<sub>2</sub>O + O-atom reaction rapidly reacts with the excess O-atoms to form CH + OH also.<sup>21</sup> The CH can further react with the O<sub>2</sub> to form OH(A).<sup>22</sup> The observed dependence of the

OH(A) intensity with the [O<sub>2</sub>] used (see Figure 9) was consistent with that expected from a kinetic simulation of the above reaction steps. Note that in the absence of O<sub>2</sub>, the main loss mechanism for CH would be via its fast reaction with O-atoms.<sup>23</sup> This reaction, in principle, can also produce CO-chemiluminescence with an emission threshold at ~ 163.8 nm. We plan to look for CO-chemiluminescence in this reaction in the absence of CH<sub>2</sub> (or C<sub>2</sub>O) plus O-atom interference(s).<sup>19</sup>

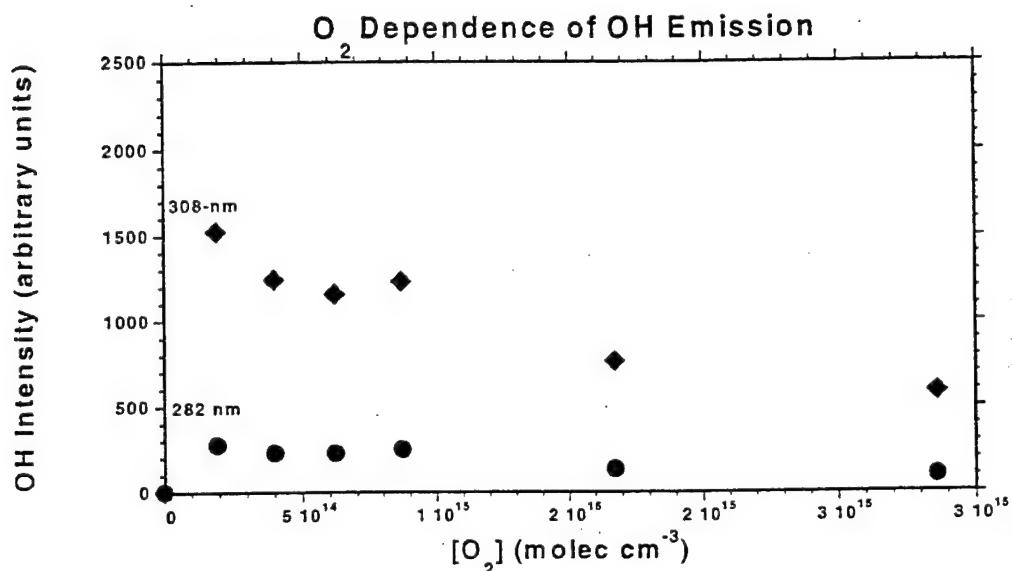


FIG. 9. Dependence of the OH(A) intensity as a function of the O<sub>2</sub> concentration employed in the flow-tube.

#### Ketene photolysis work

The time behavior of the emission in Figures 10 and 12 is consistent with the direct formation of excited CO in the reaction of the photodissociation product of ketene and O-atoms. The fast rise in the signal corresponds to the short-lived nature of the emitting states. The rate of decay in the signal at long times was exponential and found to be directly proportional to the O-atom density. The slow rise in signal of Figure 11 is consistent with the meta-stable nature of the CO(a) emitting state,

which may either form directly in the O-atom reaction or via cascading from the higher (a') and (d) states which are short lived ( $\tau_{\text{rad}} \sim 6 \mu\text{-sec}$ ) and emit in the visible.

It is well established that 351-nm photolysis of ketene produces the ground-state CH<sub>2</sub> radical.<sup>20</sup> If the CH<sub>2</sub> + O-atom reaction is responsible for the emissions of Figures 10, 11, and 12, then a linear dependence of the emission intensity with the laser fluence is to be expected. In Figure 14, the 165-nm signal shows a (laser fluence)<sup>1.4</sup> dependence,

indicating that there is an additional precursor, X, reaction with the O-atoms involved. This precursor must have its origin in a 2-photon absorption process. We postulate the identity of X to be  $C_2O$ . If this is the case then time-resolved emissions to the blue of

the 156.6-nm threshold (for photolytic- $CH_2 + O$ -atoms) should be observable. Indeed, emission at 148 nm was seen in the photolysis experiment with a fast rise time ( $< 10 \mu\text{-sec}$ ). Its intensity showed a  $(\text{laser fluence})^{2.2}$  dependence.

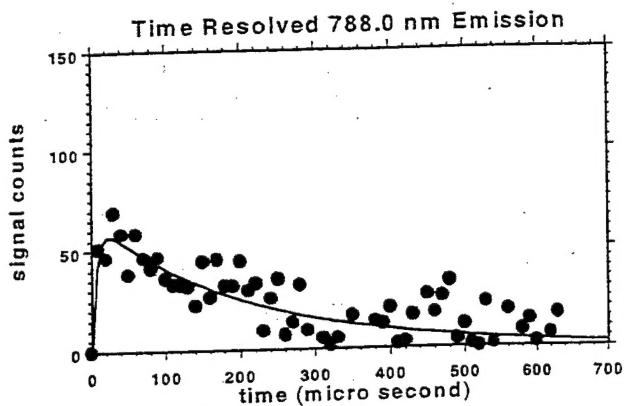


FIG. 10. Transient 788-nm emission during 351-nm  $C_2H_2O$  photolysis in excess O-atoms.

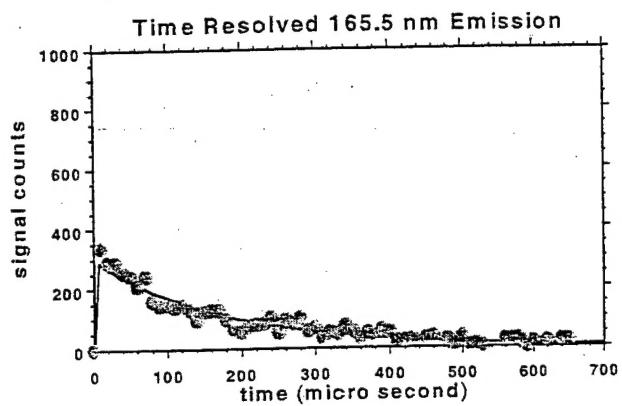


FIG. 12. Transient 165-nm emission during 351-nm  $C_2H_2O$  photolysis in excess O-atoms.

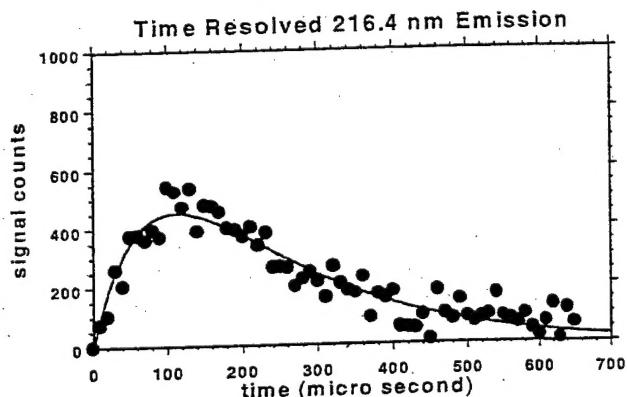


FIG. 11. Transient 216-nm emission during 351-nm  $C_2H_2O$  photolysis in excess O-atoms.

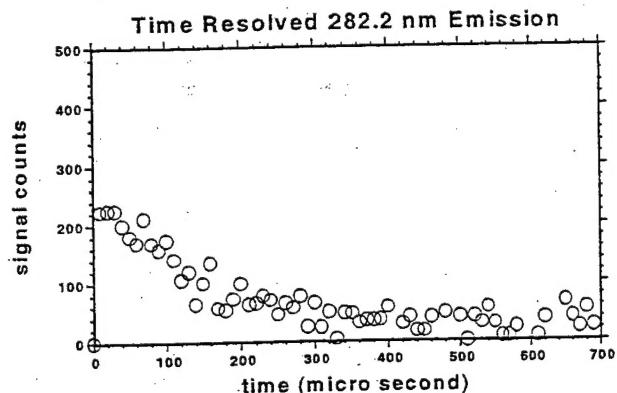


FIG. 13. Transient 282-nm emission during 351-nm  $C_2H_2O$  photolysis in excess O-atoms.

Because of the fast rise time, we further postulate that the  $C_2O$  is formed directly in the 2-photon dissociation of  $C_2H_2O$ . Another source for  $C_2O$  could be the  $HCCO + O$ -atom reaction, where  $HCCO$  forms in the 2-photon dissociation of ketene.

However, if this was the principal source for  $C_2O$ , then a relatively slow rise in the 148-nm signal would be expected since the rate of the  $HCCO + O$ -atom reaction would determine the growth rate of  $C_2O$  in the reactor.

The photolysis experiment also allowed us to further verify that the source of OH(A) emission in our experiments is the  $\text{CH} + \text{O}_2$  reaction. The rise time of the 282-nm-OH signal in Figure 13 was consistently slower than that of the 165-nm-CO signal. Furthermore, the 282-nm-OH signal intensity varied linearly with the photolysis fluence employed

(see Figure 15). This is consistent with the notion that the photolytic- $\text{CH}_2$  concentration varies linearly with the 351-nm laser intensity and therefore the CH yield through the  $\text{CH}_2 + \text{O-atom} \rightarrow \text{CH} + \text{OH}$  reaction.

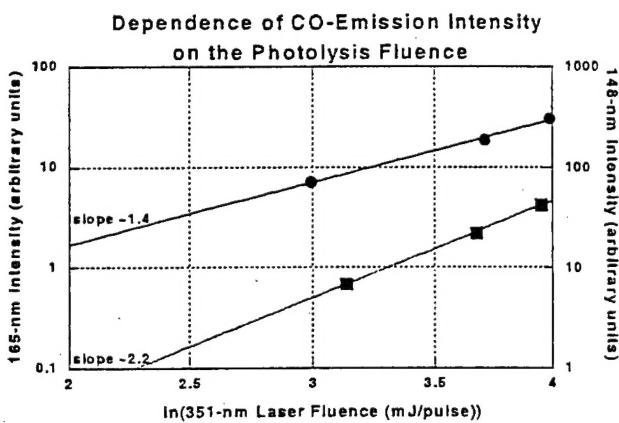


FIG. 14. The dependencies of the 148-nm- and 165-nm-CO emission intensities with the 351-nm laser fluence employed during  $\text{C}_2\text{H}_2\text{O}$  photolysis in excess O-atoms. The laser beam was focused at the center of the detection zone to improve the signal level of the CO-chemiluminescence.

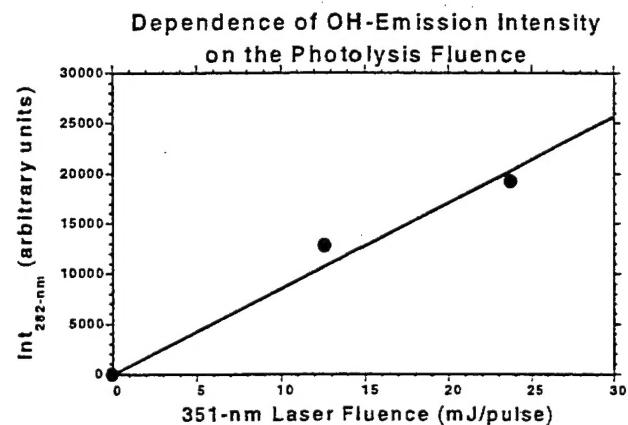


FIG. 15. Linear dependence of the 282-nm-OH emission intensity with the 351-nm laser fluence employed during  $\text{C}_2\text{H}_2\text{O}$  photolysis in excess O-atoms. An unfocused laser beam is used in the photolysis.

## CONCLUSIONS

The interference from the  $\text{C}_2\text{O} + \text{O}$  reaction in our  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  flow-tube setup, and in the high-fluence 351-nm laser photolysis of  $\text{C}_2\text{H}_2\text{O}$  in excess O-atoms has prevented us from uniquely assigning the observed CO-chemiluminescence to the  $\text{CH}_2 + \text{O-atom}$  reaction. However, the intermediate, i.e. between linear and quadratic, dependence of the 165-nm-CO emission intensity on the photolysis fluence employed does indicate that the  $\text{CH}_2 + \text{O}$  reaction may have a CO-chemiluminescence reaction channel. We plan<sup>19</sup> to improve the sensitivity of our apparatus for CO-chemiluminescence detection, and then carry out low-fluence 351-nm photolysis of ketene (to suppress any 2-photon processes) and then verify the linear dependence of the CO-emission intensity with the photolysis fluence employed.

This work has also shown for the first time that  $\text{C}_2\text{O}$  can form in the 2-photon 351-nm dissociation of  $\text{C}_2\text{H}_2\text{O}$ . We have also shown that  $\text{C}_2\text{O}$  is a possible product in the  $\text{C}_2\text{H}_2\text{O} + \text{O-atom}$  reaction. Direct LIF detection of  $\text{C}_2\text{O}$  in these two setups are currently underway.<sup>19</sup> Finally, the observation of OH(A) chemiluminescence in these experiments provide evidence for the  $(\text{CH} + \text{OH})$  product channel in the  $\text{CH}_2 + \text{O}$  reaction.

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